

## Chemical Analysis of Impact Material on a Dust Collector Flown on the MIR Space Station

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Low density silica aerogel collectors have been flown on earth-orbiting satellites to collect samples of earth-orbital debris and interplanetary dust in order to characterize the flux and types of small particles in the near-earth environment. This effort has three objectives:

- 1) to determine the relative contributions of man-made orbital debris and interplanetary dust to the flux,
- 2) the chemical analysis of the man-made debris to infer the sources of the most abundant types of particles which may be hazardous to earth-orbiting spacecraft, and,
- 3) the chemical analysis of interplanetary dust particles which have never resided in the stratosphere as a monitor of possible stratospheric contamination of the interplanetary dust particles collected by NASA from the earth's stratosphere.

High-velocity (km/sec) particles penetrate the aerogel, leaving a cone-shaped damage track, sometimes having a surviving particle at the end (as shown in Figure G-1). In 20 mg/cc density aerogel a hypervelocity particle will typically produce a track whose length is about 1000 times the diameter of the particle. Thus, a 10 micrometer diameter particle will stop in a distance of about 1 centimeter. Depending on the entry angle of the particle relative to the aerogel

surface, a 10 micrometer diameter particle may stop as deep as 1 centimeter below the surface, with a typical depth of ~0.5 centimeters.

Previously, chemical characterization of these



Figure G-1. Image of a high-velocity particle captured in low-density silica aerogel.

captured particles has required their removal from the aerogel. The penetration depth of the analysis electron beam in instruments such as electron microprobes is inadequate for the analysis of particles buried millimeters to centimeters beneath the surface of the aerogel. However, high-energy x-rays are not readily absorbed, and the inherent limitation on in-situ analysis of particles beneath the aerogel surface results from the absorption of the fluorescence x-rays. We have developed an *in situ* analysis technique<sup>[1]</sup>, performing x-ray fluorescence elemental analysis using the X-Ray Microprobe on Beamline X26A of the National Synchrotron Light Source, to characterize the heavy elements in particles at depths of up to several centimeters in low density aerogels. The aerogel is composed mostly of Si, but trace amounts of Ti, Fe, Cu, and Zn are also present. Thus, the composition

of particles or their residue is inferred by observing significant excesses in these elements over the signal from adjacent regions of the aerogel.

The X-Ray Microprobe on Beamline X26A (and previously on Beamline X26C) has been used for the chemical analysis of interplanetary dust particles collected by NASA stratospheric sampling aircraft for the past decade<sup>[2]</sup>. The chemical compositions of more than 200 interplanetary dust particles have been measured, and these provide a basis for comparison with particles captured in earth orbit. The most abundant type of interplanetary dust collected from the Earth's stratosphere is similar in chemical composition to the chondritic meteorites. Chondritic material has an Fe/Ni ratio of about 17, quite distinct from the much higher Fe/Ni ratio in terrestrial surface rocks. We use this Fe/Ni ratio to identify likely interplanetary dust particles. This identification is not perfect, since stainless steel orbital debris could also have high Ni. Some types of orbital debris, such as Ti-rich paint flakes, can also be identified on the basis of their chemical composition.

Thus far, we have examined five pieces of aerogel, each having a surface area of about 1" by 2", exposed for 18 months on the MIR Space Station. Two contained a series of parallel tracks, several having particles at the end, indicating a "swarm" of particles struck the aerogel simultaneously. All 14 of the tracks in these two swarms

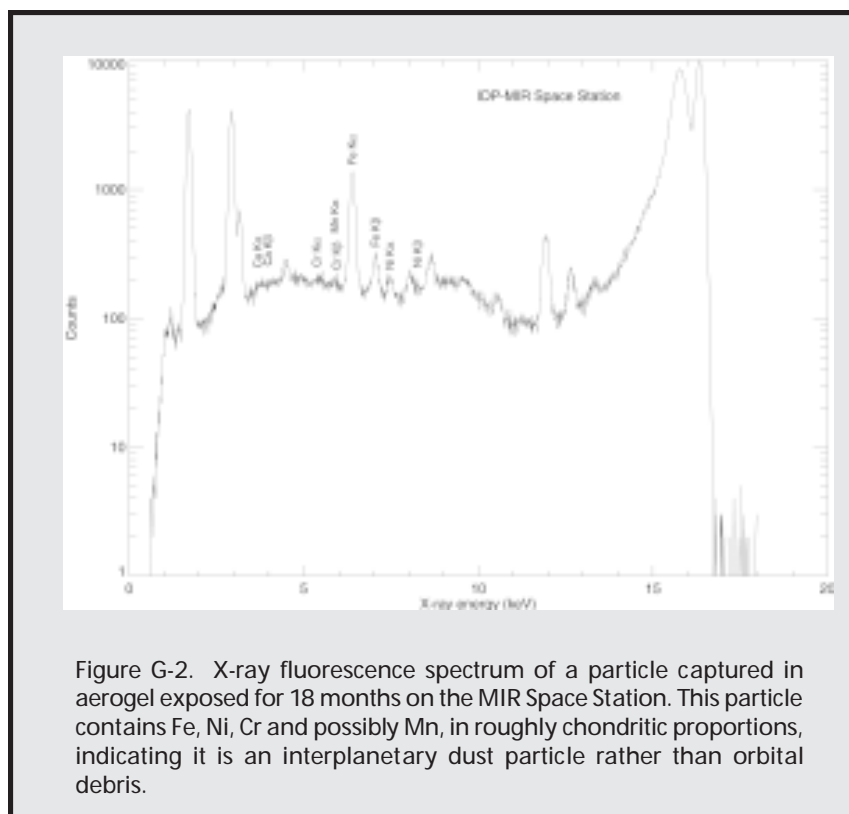


Figure G-2. X-ray fluorescence spectrum of a particle captured in aerogel exposed for 18 months on the MIR Space Station. This particle contains Fe, Ni, Cr and possibly Mn, in roughly chondritic proportions, indicating it is an interplanetary dust particle rather than orbital debris.

contained Fe residue, either distributed along the track or in particles at the end of the track. In three cases we also detected Ni in the residue or particles, with an Fe/Ni ratio similar to the chondritic meteorites. The largest of these particles, several micrometers in size, had detectable Fe, Ni, Cr, and possibly Mn, present in roughly chondritic proportions (Figure G-2). This composition provides an almost certain identification of this particle, and the other particles in this swarm, as extraterrestrial. Further analysis of these swarm particles is in progress.

We also analyzed an apparent particle at the end of a track not associated with a swarm. No elements were detected in this particle. Because this particle was several millimeters below the aerogel surface, Ca was the lightest element we would expect to detect. The apparent particle might simply be compacted aerogel at the end of the track, or it might be composed predominately of Si (which cannot be detected because of the Si signal from the aerogel) or of elements lighter than Ca.

Other impacting material produces shallow pits in the aerogel, sometimes with debris from the impacting particle on the bottom or walls of the pit. The residue in these pits was also characterized using the X-Ray Microprobe. We examined three aerogel pieces which contained pits. One pit showed K and Ca in the bottom, consistent with the impact of human waste. Examination of two other pits showed no element enhancements,

suggesting that either the impactor consisted predominately of low-Z material (lower than Al), which we cannot detect with the X-Ray Microprobe, or silicon, or that little residue from the impacting particle was retained in the these pits.

This *in situ* analysis of particles captured in aerogel also serves to develop and demonstrate analytical techniques that will be important for NASA's upcoming STARDUST mission. STARDUST, which is scheduled for launching in February 1999, carries a large aerogel collector that will fly through the dust cloud of Comet Wild-2, with a relative velocity of about 6 km/sec,

collecting more than 1000 cometary dust particles larger than 10 micrometers in size. The rear surface of the aerogel will be exposed during the cruise-phase of the STARDUST mission in an effort to collect hundreds of 0.5 micrometer size interstellar dust grains. The STARDUST aerogel collector is scheduled to return to Earth in 2006. Because the removal of individual particles from the aerogel would be tedious, and would leave open the possibility of contamination during extraction, *in situ* particle characterization, using and X-ray Microprobe, is likely to be an important part of the preliminary characterization of these particles. ■

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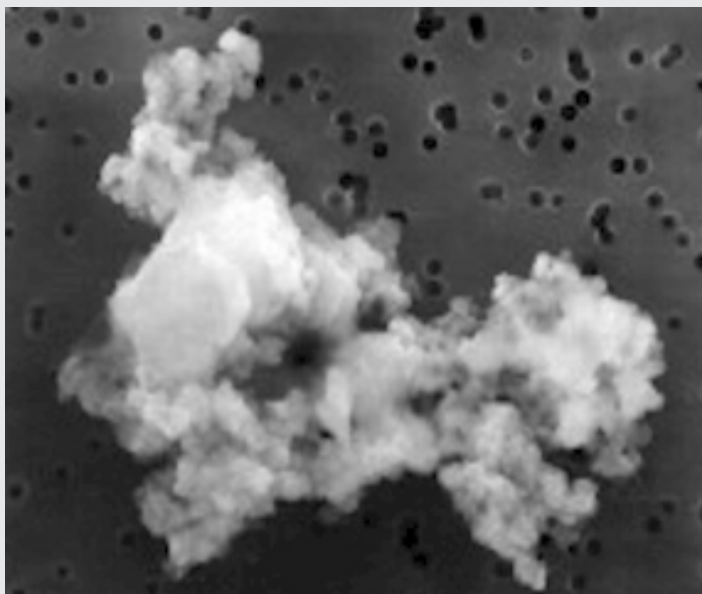


Figure G-3. IDP (~10 mm) collected from the stratosphere showing the aggregated, porous texture (NASA/JPL/Caltech).

# Comparative Rheology of Mantle Phases

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The mineralogy of the Earth's mantle changes with depth owing to pressure induced phase transformations. Olivine, pyroxene and garnet are expected to be the stable minerals in the upper 400 km of the mantle; garnet, wadsleyite and ringwoodite likely dominate the region from 400 - 700 km depth; and perovskite and ferropericlase are the stable phases at depths greater than 700 km. Rheological properties of the relevant minerals are important for defining dynamic earth phenomena such as mantle convection and the origin of deep earthquakes. Using a newly developed in-situ high pressure x-ray diffraction technique at X17B<sup>[1,2]</sup>, we have measured rheological properties of the predominant mantle phases at elevated pressure (to 20 GPa) and temperature (to 1300K).

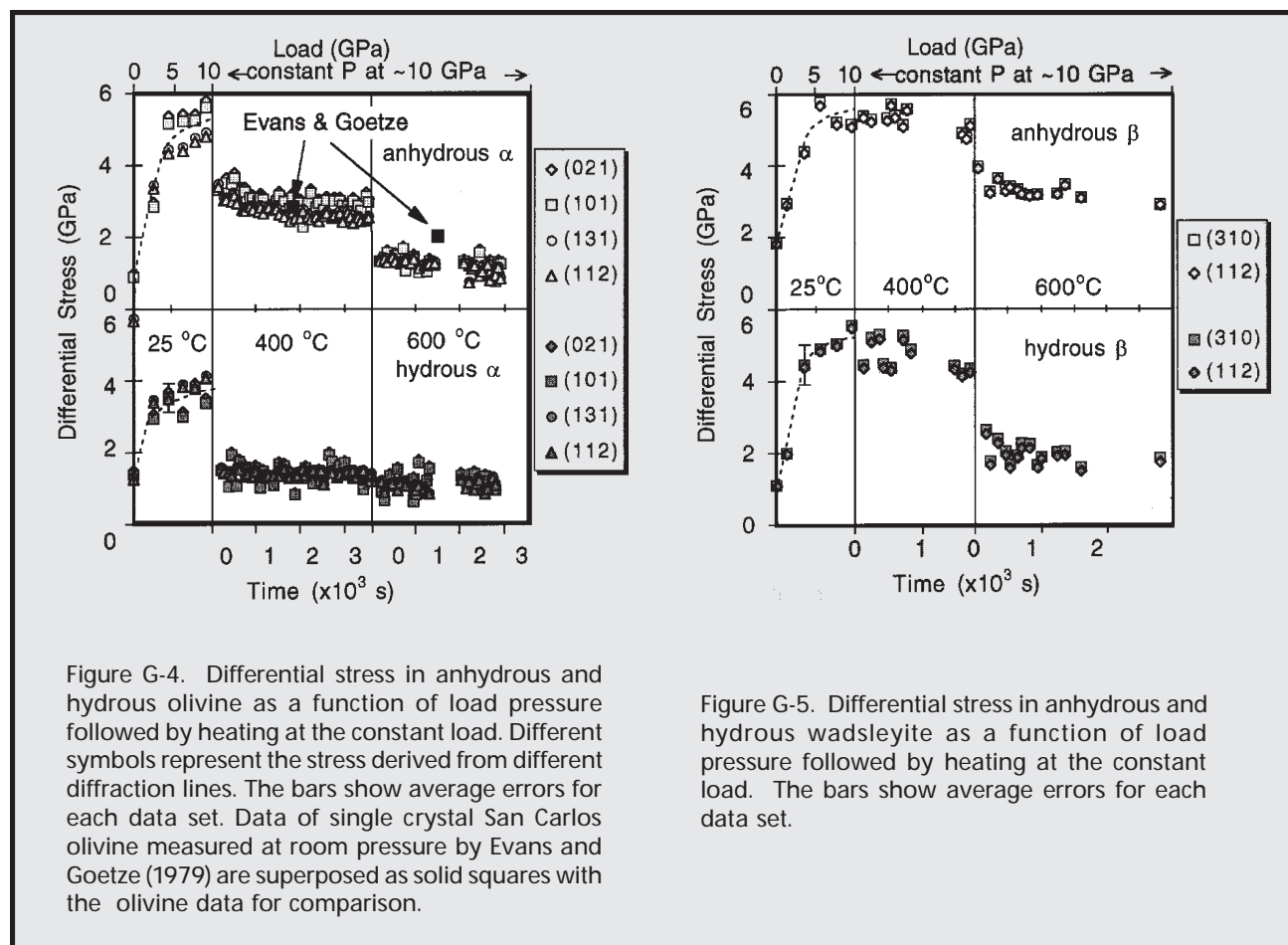
Stress held in the powdered sample is measured as a function of pressure, temperature and time by monitoring the x-ray diffraction line profile. The line broadening is

generally caused by either elastic strain or small grain size<sup>[3,4]</sup>

$$B^2 = [K(1/2)hc / (P \sin \theta_0)]^2 + [2\epsilon E]^2$$

where B represents the line breadth (refers to full width at half maximum of a gaussian profile in our experiments),  $K$  is the Scherrer constant,  $h$  is Planck's constant,  $c$  is the velocity of light,  $P$  is the average crystallite size,  $2\theta_0$  is the fixed scattering angle,  $\epsilon$  is the upper limit of strain (refers to elastic shear strain in our experiments), and  $E$  is the x-ray photon energy. Product of the aggregate Young's modulus of the mineral and the measured strain derived from above expression yields the deviatoric stress supported by the sample.

The experiments are conducted in the multi-anvil high pressure apparatus, SAM85<sup>[5]</sup>. Deviatoric stress is generated through the interaction of individual grains of the sample. Stress relaxation measurements are



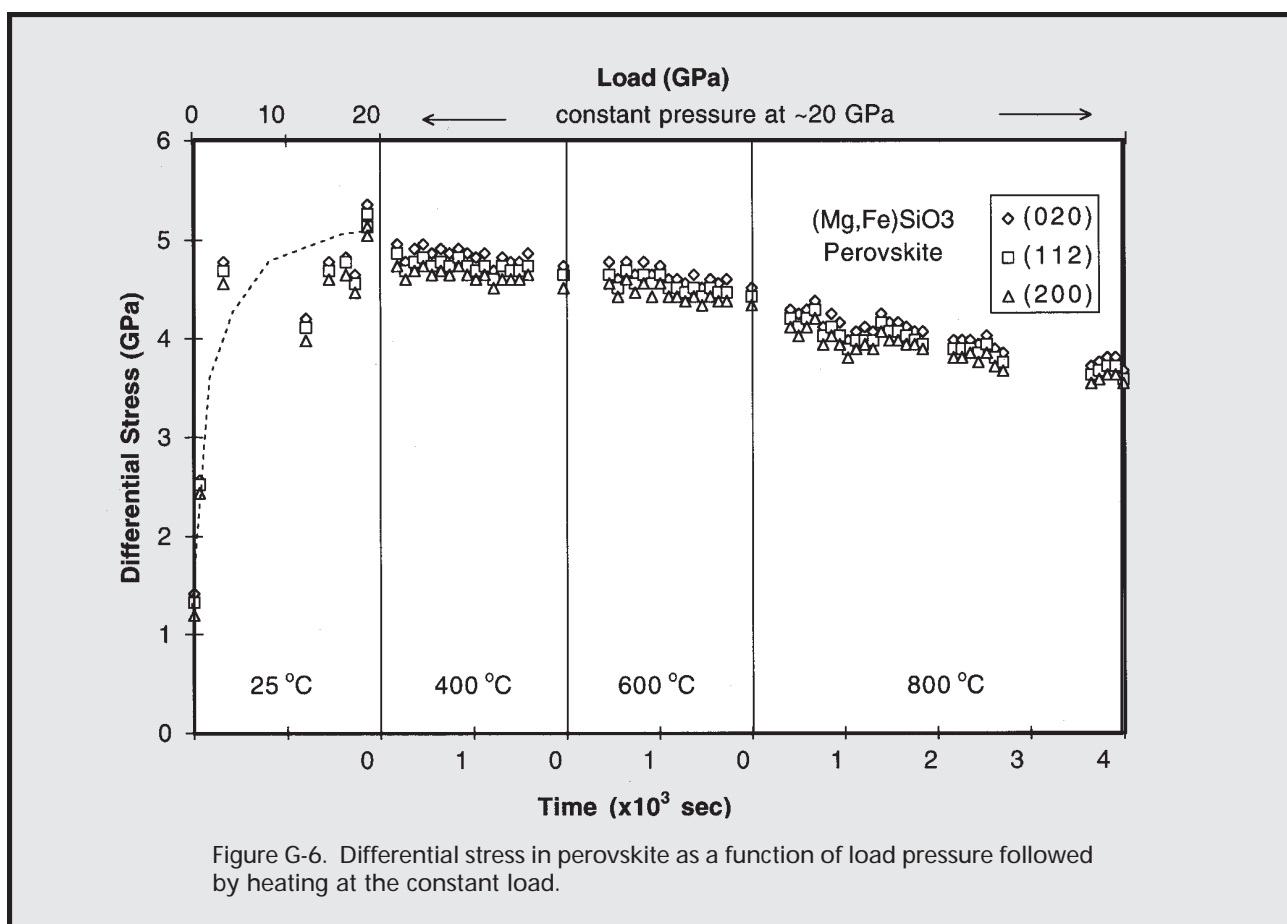


Figure G-6. Differential stress in perovskite as a function of load pressure followed by heating at the constant load.

accomplished by observing the decay of stress-induced diffraction-peak broadening as a function of time and temperature. The minerals we have studied are olivine, wadsleyite, ringwoodite, garnet, perovskite and periclase. Hydrous phases of olivine, wadsleyite, ringwoodite are also studied to investigate the water weakening on the rheological properties of minerals in the mantle. The experiments are carried out by first compressing the sample at room temperature, then stepping up and holding the temperature at desired interval for the stress relaxation measurements.

Figure G-4 illustrates the experimental result on anhydrous and hydrous olivine. The deviatoric stress in both anhydrous and hydrous phases increases with applied pressure at room temperature until the room-temperature yield strength is reached. The stress in the hydrous phase saturates at a lower level than that in the anhydrous phase, which shows that the hydrous phase is weaker at room temperature. At an applied pressure of 10 GPa the yield strength of the hydrous  $\alpha$  is about 28% less than that of the anhydrous phase. When the samples are heated up to 400°C, thermal yielding results in significant stress drop in the both phases. The hydrous  $\alpha$  shows again weaker behavior than the anhydrous phase, and the yield strength of the hydrous  $\alpha$  drops by 62% while that of

the anhydrous phase drops by 39%. Upon heating to 600°C, the yield strength of the anhydrous  $\alpha$  drops further to about the same strength level of hydrous phase, and the hydrous phase does not show any obvious decrease in yield strength. The anhydrous olivine shows stress relaxation as a function of time at temperatures of 400°C and 600°C. Yield strength data from single crystal San Carlos olivine at room pressure by Evans and Goetze<sup>[6]</sup> are superposed on the figure showing that our data agree well with theirs at low temperature.

In contrast to olivine, its higher pressure - deeper depth phases, wadsleyite and ringwoodite, are much stronger than olivine and similar to each other. Furthermore, water only slightly weakens wadsleyite and ringwoodite while weakens olivine dramatically. Figure G-5 shows the result of wadsleyite.

The rheological property of garnet is comparable to wadsleyite and ringwoodite, and periclase is as weak as olivine. Standing out of all these phases, perovskite is by far the strongest phase. In the range of investigation, temperature doesn't result in any significant stress drop as seen in the other phases. It only changes the relaxation rate. The stress at 800°C remains as high as 75% of that at room temperature at 20 GPa (Figure G-6).

Figure G-7 shows a summary of the stress capacity of the predominant mantle phases at the indicated temperatures. The temperature-depth profile of this figure is similar to that expected in a subduction zone where cold material is sinking and where deep earthquakes occur (to depths of 700 km). The general conclusion is that olivine and periclase are by far the weakest phases, with majorite, wadsleyite, and ringwoodite of comparable, but intermediate strength, and perovskite is significantly the strongest of all. The experiments represent the first high

temperature measurement of the rheological properties of most of these materials. The results suggest that the bimodal distribution of earthquake activity with depth and the cessation of earthquakes at 700 km is simply a reflection of the strength dependence and stress relaxation character of the stable phases and thus does not require different triggering mechanism for earthquakes above and below 400 km. The experimental observations are also consistent with a significant viscosity increase at the upper mantle-lower mantle boundary. ■

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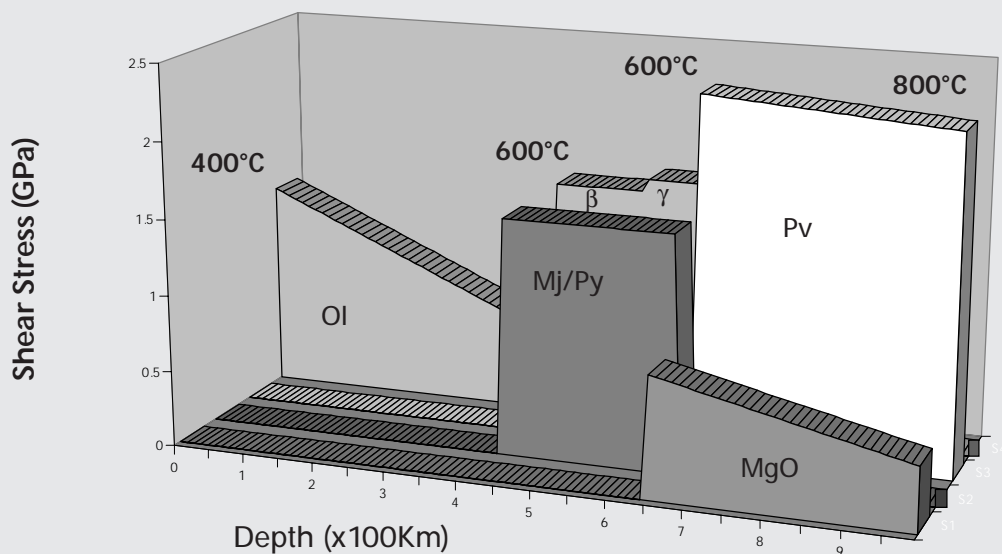


Figure G-7. Shear strength of predominant mantle phases at indicated temperature. The depth represents where the minerals are stable in the earth. Ol: olivine, β: wadsleyite, γ: ringwoodite, Mj/Py: majorite pyrope (1:1) garnet, Pv: perovskite.



# Iron in Martian Meteorites: Microanalyses of $\text{Fe}^{3+}/\Sigma\text{Fe}$ by Synchrotron MicroXANES (SmX) as Indicators of Variable Oxygen Fugacity

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Igneous rocks from Mars are believed to be sampled by SNC or martian meteorites. Martian magmatism is inferred to have produced basaltic and more evolved magmas from a peridotitic mantle<sup>[1,2]</sup>. These rare meteorites cannot be realistically sampled for destructive measurements of  $\text{Fe}^{3+}/\Sigma\text{Fe}(\text{Fe}^{2+}+\text{Fe}^{3+})$  which is used as a proxy for the oxygen budget of the planet, so that nondestructive microanalysis is essential for improved understanding of this important parameter. Variation of oxygen fugacity ( $f\text{O}_2$ ), causes compositional diversity among terrestrial magmas<sup>[3,4]</sup> and the ratio  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  is used as a monitor of oxygen fugacity, particularly when applied to coexisting minerals. Ultimately  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  provides a fundamental constraint on the abundance oxygen, this most abundant element (volumetrically) in any crust and mantle of all the rocky planets. The few reliable measurements of  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  in Martian meteorites were done on bulk samples and are difficult to apply to the crystallization history of the rocks because weathering effects complicate the results<sup>[5]</sup>. Partitioning data for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  among the coexisting minerals are needed to determine fugacity sensitive magmatic equilibria for Martian rocks. Here we provide *in situ* microanalyses of  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  using the XANES microprobe at X26A for minerals in eight meteorites that may be used to estimate oxygen fugacity in Martian crustal rocks. The data are comparable with those from terrestrial rocks buffered at the quartz-magnetite-fayalite and nickel - nickel oxide reactions and are distinct from products of asteroidal magmatism buffered by iron-wüstite reaction<sup>[6,7,8]</sup>. The results indicate that the crust of Mars is relatively oxidized and comparable with that of the Earth. The results reflect Martian magmatism, shock effects and probably hydrothermal activity.

To document oxygen fugacity related equilibria among coexisting minerals,  $\text{Fe}^{3+}/\Sigma\text{Fe}$  data for each mineral being considered must be acquired at petrologically constrained locations on mineral grains. Ninety three spectra of the Fe K-absorption edge (Figure G-8) were acquired using Synchrotron microXANES (SmX) spectroscopy for 12x15 micrometer areas on coexisting

olivine, pyroxene, plagioclase/maskelynite, oxides, and carbonate in petrographic thin sections of eight Martian meteorites: ALH77005, ALH84001, Chassigny, EET79001, LEW88516, Nakhla, Shergotty and Zagami. The spectra were processed to extract quantitative estimates of  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . Sm measurements were made using the X-ray fluorescence microprobe facility (beamline X26A) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The spatial resolution

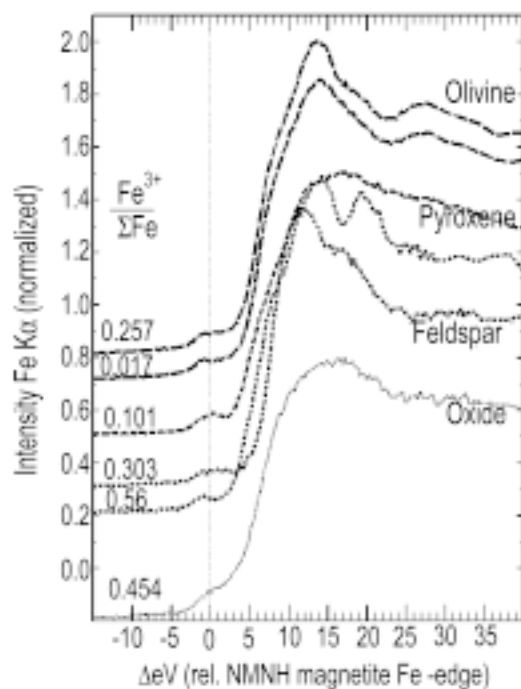


Figure G-8. Representative synchrotron microXANES spectra of the Fe-K edge in: two olivines from LEW88516, pyroxene from m ALH77005 and Zagami, feldspar and oxide from Zagami. All spectra are normalized to Intensity = 3D 1.0 at +40eV but are displaced vertically for clarity. The line at  $\Delta\text{E}=3\text{D}0$  represents the magnetite pre-edge having  $\text{Fe}^{3+}/\Sigma\text{Fe}=3\text{D}0.667$ .

of SmX permits microanalyses to be made avoiding oxide inclusions in many minerals that confound bulk analytical determinations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . The energy shifts of a pre-edge feature in the Fe K-absorption spectra are a function of oxidation state<sup>[9]</sup> and were calibrated against the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values in standard minerals<sup>[10]</sup>. SmX spectra of a broad range of rock-forming minerals from terrestrial rocks that were independently analyzed by either Mössbauer or wet chemical techniques<sup>[11,12]</sup> were also used to test the consistence of the results. The grain size of these meteorites is in the sub-millimeter range, so the spatial resolution of SmX permits variation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  to be detected within mineral grains.

**Results:** Every mineral shows variation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from meteorite to meteorite and within a single meteorite.  $\text{Fe}^{3+}/\Sigma\text{Fe}$  is lowest in olivine and highest in feldspathic phases (Figure G-9 - Table)

## OLIVINE

Meteorites ALH77005, LEW88516 and Chassigny all contain significant olivine. (Our EET79001 is from a basaltic lithology B with no olivine). Olivine is generally not a host for  $\text{Fe}^{3+}$  so  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values of 0 are normal. Colorless olivine in these meteorites contains  $\text{Fe}^{3+}/\Sigma\text{Fe}$  less 0.02. Olivine in ALH77005 and LEW88516 is both colorless and brown as a result of shock induced modifications<sup>[2]</sup>. Brown olivine has values of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  up to 0.12 in ALH77005 and 0.26 in LEW88516 in which very deeply colored healed fractures through the grains have the highest values. Mössbauer analysis 13 of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in bulk olivine from ALH77005 gave 0.045, and probably represents the average of the microscale variability seen. In Chassigny, olivine  $\text{Fe}^{3+}/\Sigma\text{Fe}$  varies from 0 to 0.16 but does not correlate with color variations. The range observed is consistent with recent TEM observations of exsolved lamellae containing iron oxides in Chassigny olivine<sup>[14]</sup>.

## PYROXENE

Pyroxene is present in all the Martian meteorites and is the most useful mineral for examining the variation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  with  $f\text{O}_2$ . In general, pyroxene in the lherzolitic meteorites has lower  $\text{Fe}^{3+}/\Sigma\text{Fe}$  than in the basaltic meteorites (Figure G-9).  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in two pyroxene species in ALH77005 varies (0.09-0.3) and may correlate with variations of Ti, Al and Cr and the pyroxene species (pigeonite or augite), but insufficient  $\text{Fe}^{3+}/\Sigma\text{Fe}$  analyses are currently available to confirm these correlations. The pyroxenites examined, Nakhla (augite) and ALH84001 (orthopyroxene), have similar  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values (0.09 - 0.14) to the lherzolitic samples. The observed values are, however, comparable with the lower part of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  range measured in mantle peridotites

and pyroxenites on Earth<sup>[7]</sup>. The observed values are typical for terrestrial orthopyroxenes (~0.1) and lower than those of clinopyroxene equilibrated at the quartz-magnetite-fayalite buffer curve.

In Nakhla, spectra of several grains and a traverse across a single grain of augite revealed homogeneous  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (0.09), similar to the bulk meteorite value<sup>[15]</sup>, except where the analysis included a micrometer scale oxide inclusion has higher  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (0.16). Analyses that overlapped grain boundaries in Nakhla showed elevated  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (0.30). The basaltic meteorites, Shergotty and Zagami, and the basaltic lithology B of EET79001 have high  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (0.2 - 0.3) consistent with their having crystallized at or above the QFM buffer<sup>[16]</sup>. Variations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in both Zagami and Shergotty may reflect steric differences between coexisting pigeonite and augite in these meteorites, but may also suggest that pigeonite has variable  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in both meteorites. Eucritic pigeonite, from asteroidal basalts, is dominated by  $\text{Fe}^{2+}$  as expected from the inferred oxygen fugacity at or below the iron-wüstite buffer.

## FELDSPAR

The lherzolitic meteorites ALH77005 and LEW88516 and the basaltic lithology of EET79001 have relatively constant  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (~0.31) in feldspar. The basaltic meteorites, Shergotty and Zagami, however, are more oxidized with  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ~0.48. The increase of oxidation ratio in pyroxene from the lherzolitic to basaltic meteorites is repeated in feldspar data. Compositional differences between the maskelynite in EET79001 lithology B and that of the basaltic meteorites suggest that the coupled substitution  $\text{Na}+\text{Si}=\text{3D Ca}+\text{Al}$  may have altered the abundance of sites most compatible with  $\text{Fe}^{3+}$  (Al) and  $\text{Fe}^{2+}$  (Ca) in plagioclase and that the feldspar results may reflect crystal chemical controls in addition to oxygen fugacity effects. Insufficient spectra are presently available to test this possibility and to document compositional variation within individual meteorites.

## OTHER MINERALS

Oxide spectra from Nakhla suggest  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values of 0.4 -0.5 similar to the previous calculated results<sup>[17]</sup>. The low intensity of the pre-edges of the Fe-XANES spectra suggest that the oxide minerals have little tetrahedrally coordinated Fe. The oxide minerals may be exsolved ilmenite-hematite solid solutions. Iddingsite spectra from Nakhla appear to be dominated by this oxide and give  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of 0.45. A preliminary calcite spectrum for ALH84001 suggests  $\text{Fe}^{3+}/\Sigma\text{Fe}$  at 0.14. Discussion: There are three independent processes that may have controlled the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of the Martian meteorites: (1) oxidation caused by magmatism in a relatively oxidized



magmatic system. (2) hydrothermal alteration and (3) shock induced effects. Detailed  $\text{Fe}^{3+}/\Sigma\text{Fe}$  measurements on coexisting phases and correlation of the oxidation state results with other microanalytical and crystallographic data will be needed to distinguish among these processes.

The general trend of increasing  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from the peridotitic samples to the basaltic samples suggests that magmatism on Mars became more oxidized as it evolved (again comparable to much terrestrial magmatism) and is consistent with the presence on the modern Martian surface of abundant ferric oxide minerals<sup>[18]</sup>. Highly fractionated silicates discovered by Pathfinder/Sojourner at Sagan Memorial Station on Mars 1 should have high  $\text{Fe}^{3+}$  in pyroxene and feldspar and we anticipate that SmX measurements on returned samples, when available, will confirm this prediction. It is unlikely that magmatism is the only contributor to the range of oxidation in the Martian suite. Shergotty and Zagami are young and may have erupted on a (partially) dewatered planet. The mantle from which they were extracted may well have been wet and capable of oxidizing the magmas. Old meteorites such as ALH84001 sample lithologies may have formed when Mars had extant surface water and hence had a significantly wetter mantle. The role of water in the formation, dehydrogenation and metasomatism of peridotitic and pyroxenitic rocks in the terrestrial mantle is increasingly recognized<sup>[19]</sup> and is an important target for Martian studies. The roles of both hydrothermal

activity and shock modification of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  may be important. Both ALH77005 and LEW88516 experienced major shock events that generated abundant defects in the olivine.

The textures observed in olivine of these lherzolites are consistent with post shock annealing seen in experimental charges<sup>[20]</sup>. The brown color in this olivine may result from light scattering from the defects, oxidation of the defects, or both. The Martian atmosphere is oxygen poor ( $p\text{O}_2 \sim 10^{-6}$ ) so any shock induced oxidation probably involved other oxygen bearing species - perhaps atmospheric  $\text{CO}_2$ . Water present in the Martian crust when ALH77005 was shocked may provide an alternate oxidizing agent. The time of oxidation is, however, uncertain. The presence of significant amounts of water in the Martian crust make hydrothermal processing of some crustal rocks seem very likely. In ALH77005, crystalline feldspar rims replacing the shock produced maskelynite glass, strongly implies a period of extended subsolidus heating of this rock during which hydrothermal interactions might have occurred. In LEW88516, the presence of deeply colored, healed fractures in olivine requires more localized oxidation processes than in ALH77005 and suggests that the olivine was first shocked, and then oxidized during a hydrothermal recrystallization event caused by the flux of an oxidizing agent through cracks. The absence of tight temperature constraints and of data for the coexisting magmas and fluids that equilibrated with the Martian meteorites prevents the

Figure G-9. (Table) Synchrotron microXANES analyses of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in minerals from Martian meteorites.

Meteorite	Olivine	Pyroxene	Feldspar	Oxide	Others
Shergotty	n.p.	$0.28 \pm 0.05$	$0.47 \pm 0.10$	<i>na</i>	
Zagami	n.p.	$0.212 \pm 0.08$ ( $0.171 \pm 0.04$ )	$0.49 \pm 0.08$	<i>na</i>	
Nakhla	<i>na</i>	$0.09 \pm 0.01$ clean '0.17 – 0.35' cloudy	<i>na</i>	0.49	Iddingsite $0.42 \pm 0.05$
Chassigny	0.06 - 0.16	0.35	<i>na</i>	<i>na</i>	
ALH77005	0 - 0.05 clean 0.12 brown	0.09 – 0.30	0.32	<i>na</i>	
EET79001	<i>na</i>	0.27 – 0.3	$0.32 \pm 0.05$	<i>na</i>	
LEW88516	0 - 0.03 clean 0.11 - 0.26 brown	<i>na</i>	$0.30 \pm 0.07$	<i>na</i>	
ALH84001	<i>na</i>	$0.14 \pm 0.01$	<i>na</i>	<i>na</i>	cc 0.14

n.p.=not present, *na*=not analyzed

determination of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  partition coefficients from the present results. However, the data confirm the general trends of partitioning for ferric and ferrous in terrestrial magmatic systems and appear to be consistent with oxygen fugacities ranging from below the buffer curve quartz-fayalite-magnetite to about that of the nickel-nickel oxide buffer. These data provide the first petrologically constrained sampling of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from any meteorite parent body. They differ from bulk

measurements of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  as the difficulties caused by contaminants such as weathering products and micrometer scale inclusions are easily excluded. The results for the Martian suite are generally consistent with the formation of these rocks in a very "terrestrial", i.e. oxidized, setting. The range of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  seen is comparable to that seen in many mantle and eruptive rocks on Earth. Martian samples are much more oxidized than lunar, basaltic achondrite and most chondritic meteorites. ■

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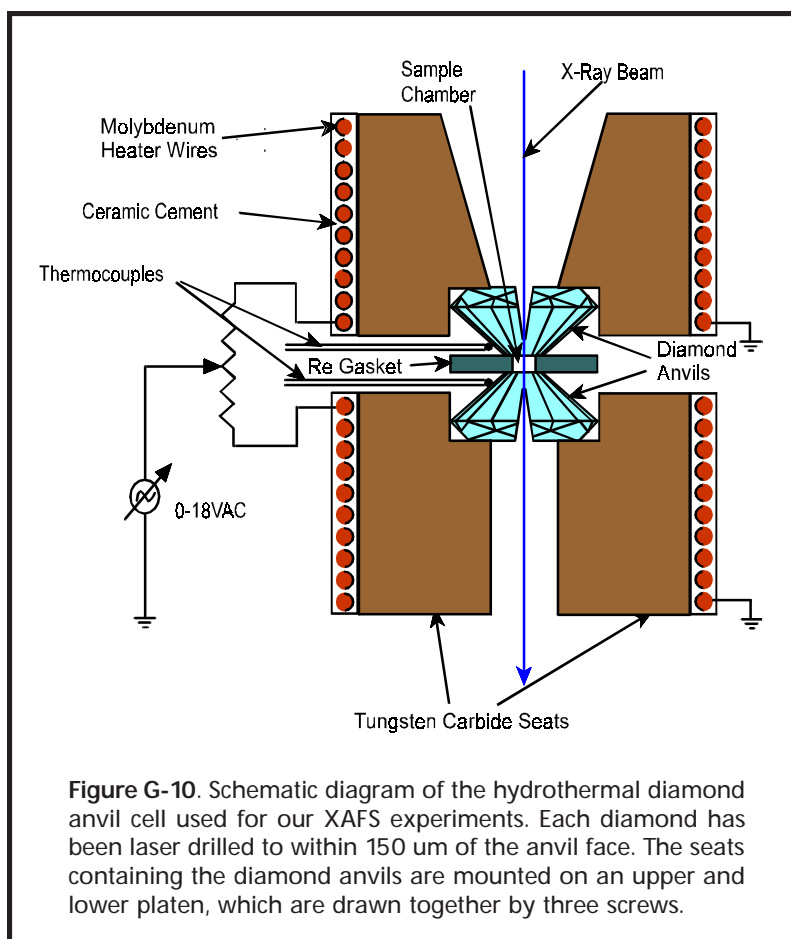
# First XAFS Measurements on Ferrous Chloride Hydrothermal Solutions using a Novel Diamond Anvil Cell

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The decrease in density, viscosity, and dielectric constant of water with temperature signals that appreciable changes take place in its structure under sub- and supercritical conditions. Very little is known about how such changes in the physical properties of water, in going from ambient to supercritical conditions, influence the nature of short-ranged interactions between solvated ions. Determination of the structure and speciation of complex ions in hydrothermal solutions under controlled thermodynamic conditions is an essential step in developing a theoretical basis of electrolytes beyond the Debye-Hückel theory. Systems such as iron(II) chloride aqueous solutions have a two-fold interest for us: 1) Current theories of the molecular electronic structure and metal-ligand interactions for first-row transition metal ions are among the most developed<sup>[1]</sup> and thus offer an opportunity for development of an extensive knowledge base of such electrolytes, and, 2) they have direct relevance to studies in hydrothermal geochemistry<sup>[2,3]</sup>.

Conventional metal autoclaves have proven restrictive for studies on dissolved salts in supercritical water because of the severe corrosion problems caused by such fluids. The hydrothermal diamond anvil cell developed by Bassett *et al.*<sup>[4]</sup> offers a much more suitable alternative because corrosion problems can be greatly minimized while control over pressure, temperature, and concentration can be substantially enhanced. However, x-ray absorption experiments have been limited to the higher photon energies (> 15 keV) because of the attenuation of the beam by the diamonds. We have developed a new diamond anvil cell suitable for

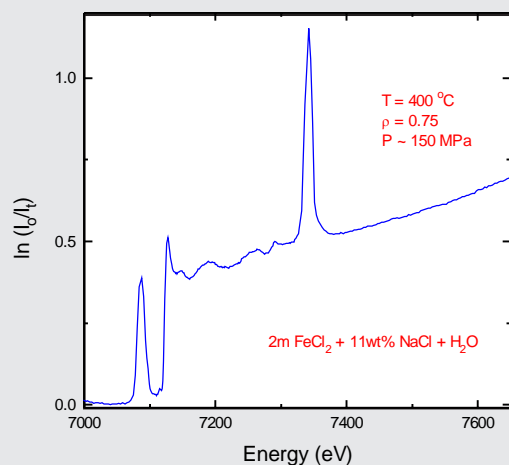
making x-ray absorption studies of first row transition metal ions in supercritical aqueous solutions. Each diamond has been laser drilled to within 150 micrometers of the anvil face, minimizing the loss of x-ray intensity due to absorption and scatter by diamond. We have for the first time measured Fe K-edge X-ray Absorption Fine Structure (XAFS) spectra from 2m Fe(II)Cl<sub>2</sub>/NaCl/H<sub>2</sub>O solutions, at temperatures ranging from 25-500°C and pressures estimated up to 200 MPa, using the microprobe capabilities of beam line X26A. The capabilities of the



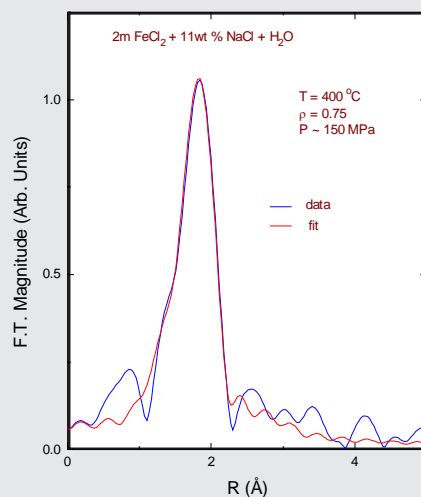
new diamond anvil cell were demonstrated more fully in a previous XAFS study made on zinc chloride aqueous solutions, at beam line B-2 of the Cornell High Energy Synchrotron Source (CHESS), at temperatures ranging from 25-650°C and pressures up to 800 MPa. The solution samples were placed inside a volume defined by a 0.5 mm hole, of a 0.13 mm thick rhenium gasket, and the opposing diamond anvil culet faces pressing against the hole. The measurements were made in transmission mode, using conventional gas ionization chambers. The incident x-ray beam was focused using the Kirkpatrick/Baez mirrors to approximately 13 micrometer spot size. Selective tilting of the cell by 0.1-0.2 degrees relative to the x-ray beam caused the diffraction peaks resulting from the diamonds to shift in photon energy between individual spectra. In this way, spectral refinement can be accomplished by replacement of a region contaminated by a peak in one scan by an uncontaminated region from another scan.

Studies of this system were largely motivated by our earlier studies on the structure of iron(II) complexes in saline fluid inclusions in quartz found in a pegmatite dyke intruding into granulites of the Saxon Granulite Massif, Germany<sup>[5]</sup>. Results from fitting of the Fe K-edge spectra measured at different temperatures, where the pressure varied according to the equilibrium liquid-vapor coexistence, indicate that the iron(II) ion is predominantly

octahedrally hydrated from 25°C to 100°C. From 200°C to 500°C, there appears to be a stable mixture of chloro iron(II) complexes in the fluid, with the average ligand coordination number being 3.5. The results from a preliminary analysis of the XAFS spectra measured from 2m Fe(II)Cl<sub>2</sub>/11wt% NaCl/H<sub>2</sub>O solutions under similar pressure and temperature conditions are in qualitative agreement with our results for the fluid inclusions. This is despite the fact that the iron concentration in the fluid inclusions is considerably lower (up to several thousand ppm) than in the solutions. In addition, the Cl<sup>-</sup> concentration of the liquid phase of each inclusion undergoes a gradual increase with temperature due to the progressive dissolution of its constituent halite phase (NaCl), which is typically completely dissolved at about 260°C. There is a progressive and very similar slight change with temperature, from 200°C to 500°C, in the near edge region of the spectra measured from either the inclusions or the 2m Fe(II)Cl<sub>2</sub>/11wt% NaCl/H<sub>2</sub>O solution. This may result from the structural symmetry of the iron chloro complexes undergoing small changes with temperature. Our XAFS experiments on zinc and iron in solutions using the HDAC, including on the 2m Fe(II)Cl<sub>2</sub>/11wt% NaCl/H<sub>2</sub>O system, demonstrate that this is a very useful tool which can be used to constrain the thermodynamic variables and thereby help establish a base of knowledge to more fully understand, for



**Figure G-11.** Fe K-edge XAFS spectrum measured from a 2m Fe(II)Cl<sub>2</sub>/11wt% NaCl/H<sub>2</sub>O solution at 400°C and about 150 MPa of pressure. The large peaks occur as a result of diffraction of the incident x-ray beam from the diamond anvils of the cell.



**Figure G-12.** The magnitude of the Fourier transforms (FT) of the extended XAFS data (blue line), isolated from the spectrum shown in Figure G-11, and of the fit (red line) of this data, made using FEFF6.

example, reaction kinetics in fluid-rock interactions. When used in conjunction with similar experiments carried out on naturally occurring fluid inclusions, the knowledge of speciation and structure of metal complexes

at elevated temperatures and pressures gained from such experiments should prove to be very useful for increasing our understanding of the transport and deposition of elements under ore-forming, hydrothermal conditions. ■

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